Catalyzed cis-trans Isomerization of Polybutadienes and Polyisoprenes

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Checked by: G. S. Trick and J. M. Ryan

Where $X = \text{C}_6\text{H}_5\text{S}$ (part A) or $\text{SO}_2$ (part B). Other methods, including the case where $X=\text{Br}$, are mentioned in part D.

A. Photosensitized Isomerization of Polybutadiene in Solution

1. Procedure (Note 1)

Diphenyl disulfide (0.3 g) is dissolved in 100 ml of a benzene solution containing 1 g of cis-1,4-polybutadiene. Aliquots of the sensitized solution are placed in several Pyrex® tubes that are flushed with nitrogen and stoppered (Note 2). The tubes are placed 12 in from a General Electric H85 mercury lamp and irradiated for 6 h (Note 3).

The benzene solution is poured into a beaker (Note 4), and 100 ml of methanol is added slowly to precipitate the isomerized polymer. The precipitate is filtered, washed with methanol, and dried at 50° in a vacuum oven. The polymer structure is that of the equilibrium cis-trans ratio of 25/75 (Note 5).

2. Notes

1. This procedure is applicable to the cis-trans isomerization in solution of 1,4-polybutadiene and 1,4-polyisoprene as well as the isomerization units in copolymers.
2. An atmosphere of nitrogen is required to avoid extensive degradation of polymer that occurs when the ultraviolet irradiation is carried out in the presence of air.
3. The cis-trans ratios in the isomerizates, short of equilibrium, will depend on the placement of the tubes with respect to the ultraviolet source, on the intensity and spectral distribution of the source, and on the time of irradiation. Typical results for polybutadiene photoisomerization are shown in Table 1. The intrinsic viscosity of the isomerized polybutadiene is essentially unchanged from that of the starting polymer.
Table 1.

<table>
<thead>
<tr>
<th>Reaction Time, h.</th>
<th>trans-1,4 Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
</tr>
</tbody>
</table>

4. The photoisomerization is generally accompanied by the formation of some gelled polymer attached to the wall of the Pyrex tube. This is left in the tube when the benzene solution is decanted into a beaker.

5. The equilibrium cis-trans ratio of about 25/75 in polybutadiene is obtained starting from a nearly 100% cis- or 100% trans-polymer, whereas a nearly 100% cis- or trans-polyisoprene attains an equilibrium cis-trans ratio of about 40/60. The characterization of the microstructure is described in part C.

B. Bulk Isomerization of Polyisoprene with Sulfur Dioxide

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1. Procedure (Note 1)

Natural rubber (RSSI, pale crepe, or highly purified rubber from the United States Rubber Co.) is masticated on a two-roll laboratory mill until its Mooney viscosity at 100° is 55-60. It is then formed into sheets of approximately 0.24 cm thickness and 25 cm width. Gutta percha is formed to the same dimensions with the mill rolls at 60°. Both polymers are rolled in glazed Holland paper.

The roll of polyisoprene (~400 g) is placed in the reaction vessel, which is a glass cylinder 30 cm long, 8 cm dia., with a ground glass joint at one end, containing inlet and exit tubes for the passage of nitrogen or sulfur dioxide (Hood!) as required. The reaction vessel is immersed in an oil bath at 140±1°, and the air is removed with a stream of nitrogen. The nitrogen is then replaced by sulfur dioxide (laboratory reagent grade) from a syphon. The sulfur dioxide is preheated by passing it through a copper coil immersed in an oil bath before it enters the reaction vessel. The flow of sulfur dioxide is rapid for the first few minutes to remove the nitrogen, but it is then reduced to a slow rate for the remainder of the experiment. A continuous flow of sulfur dioxide is not necessary because it functions as a catalyst and is not consumed. This procedure is used, however, to ensure that no air enters the apparatus. Isomerization occurs gradually, and the equilibrium composition of approximately 60% trans is reached in under 24 h (Note 2).

2. Properties

Configurational changes in the double bonds of natural rubber or gutta-percha cause marked changes in the strength, stress-strain (Note 3), crystallization (Note 4), and other physical properties of their vulcanizates.6,7 The effect of isomerization is strikingly obvious in the case of gutta-percha because this normally rigid polymer is converted into a rubber-like material.7
Isomerized natural rubbers of increasing trans content have the following properties. Their processing behavior differs from that of normal natural rubber because far less breakdown occurs on cold milling.\textsuperscript{7} With pure gum vulcanizates (Note 5) tensile strength falls gradually at first but, when about 10% trans double bonds are present, a very rapid decrease occurs.\textsuperscript{6} The vulcanizate obtained from natural rubber containing about 6% trans double bonds is particularly interesting because, although its tensile strength and stress-strain properties are very similar to those of normal natural rubber, its rate of crystallization at low temperatures is several hundred times slower.\textsuperscript{6} This type of vulcanizate possesses distinct advantages over those made from normal natural rubber when used at low temperature (-10° to -40°), because under these conditions the former would retain its elasticity for many years, whereas the latter would harden and lose its flexibility in a few days.

3. Notes
1. This procedure involves the treatment of the solid polymer with sulfur dioxide and is by far the most convenient method of obtaining the isomerized polymer in sufficient quantities (about 1 lb.) to enable the physical properties to be thoroughly evaluated. Larger amounts, up to 34 lb., have been made by treatment of natural rubber with butadiene sulfone in internal mixers.\textsuperscript{8}
2. A small increase occurs in intrinsic viscosity, gel content, and bulk viscosity, measured at 100° with a Wallace Rapid Plastimeter,\textsuperscript{9} as isomerization takes place. Changes in chemical unsaturation, determined by treatment with perbenzoic acid\textsuperscript{10} are negligible\textsuperscript{6} (Table 2).
3. Tensile strengths and stress-strain properties are measured on a Goodbrand testing machine by extending Type C British Standard 903 dumb bells at 600% per minute.
4. Rate of crystallization is measured by means of the relaxation of stress in a vulcanized test piece extended 150% and maintained at -26° (at which temperature the rate is maximal). The time for reduction of stress by a factor of 2 has been shown to be an accurate measure of the time for half the primary crystallization to be achieved; stress half-life is thus an inverse measure of rate of crystallization.\textsuperscript{11}

<table>
<thead>
<tr>
<th>Table 2. Properties and Structure of Isomerized Polyisoprenes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. From Natural Rubber</strong></td>
</tr>
<tr>
<td>Reaction time, h.</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>24</td>
</tr>
<tr>
<td><strong>B. From Gutta Percha</strong></td>
</tr>
<tr>
<td>Reaction time, h.</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>24</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Measured in benzene at 25°.
\textsuperscript{b}Weight % of polymer insoluble in n-decane after 48 h of swelling at 25.0°.
\textsuperscript{c}Determined by infrared spectroscopy (see part C).
5. Vulcanizates are prepared from the isomerized polyisoprenes by compounding on a two-roll laboratory mill according to the following recipe, and heating in a press at 140\(^0\) for 30 min.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisoprene</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.5</td>
</tr>
<tr>
<td>N-Cyclohexylbenzothiazole-2-sulfenamide</td>
<td>0.7</td>
</tr>
<tr>
<td>Phenyl-2-naphthylamine</td>
<td>1</td>
</tr>
</tbody>
</table>

C. Microstructure of Polybutadienes and Polyisoprenes

1. Infrared Analysis
   In the case of polybutadiene or a butadiene-containing copolymer, the characterization of the isomerize for cis-trans content is easily performed by means of infrared analysis of a thin film cast from a benzene solution of the polymer. The analysis involves measuring the absorbance \((A)\) of the 13.6 and 10.4 \(\mu\) bands (cis and trans, -CH=C- units, respectively), and using the expression\(^{12,13}\)

\[
\% \text{ cis} = 100\left(\frac{4.4A_{13.6}}{4.4A_{13.6} + A_{10.4}}\right)
\]

This expression gives the percentage of the 1,4-polymerization units in the cis configuration, the trans content then being given by \((100-\text{cis})\). When 1,2-polymerization units (-CH=CH\(_2\) units) are present, and when the cis-trans content is to be expressed in terms of the total polybutadiene unsaturation, a more detailed infrared method may be used.\(^{14,15,16}\)

In the case of polyisoprene or an isoprene-containing copolymer, infrared analysis can be used to determine the cis-trans content,\(^ {17}\) but a simpler and more accurate analysis is based on \(^1\)H NMR spectroscopy. The infrared changes accompanying the isomerization of 1,4-polyisoprene are rather subtle, with the cis and trans -C(CH\(_3\))=C- units both having their main absorptions at around 12\(\mu\).\(^ {13}\) Analysis based on characteristic absorptions at 8.89 and 8.74\(\mu\) in Hevea and Balata, respectively, have been used, but they are not reliable for random distributions of cis and trans units.\(^ {17}\) On the other hand, infrared is often preferred over NMR for determination of 1,2- and 3,4-polymerization units, especially when these are present in small amounts.\(^ {17}\)

Infrared examination reveals that, when diphenyl disulfide is used as photosensitizer, a small amount of C\(_6\)H\(_5\)S• radical becomes permanently attached to an isomerized polyisoprene backbone, but apparently not to an isomerized polybutadiene backbone.

The photolysis of diphenyl disulfide involves the reaction:

\[
\text{C}_6\text{H}_5\text{S-SC}_6\text{H}_5\text{S•} \rightarrow 2 \text{C}_6\text{H}_5\text{S•}
\]

The incorporation of some C\(_6\)H\(_5\)S• permanently into the polyisoprene backbone is believed to involve the reaction on the next page in which two phenylsulfide units are bonded to one repeat unit of the polymer. This reaction presumably does not occur in polybutadiene. Isomerization of polyisoprene with sulfur dioxide yields a cleaner product, uncontaminated by adducts.

2. Nuclear Magnetic Resonance Analysis
   In the case of polyisoprene or an isoprene-containing copolymer, the \(^1\)H NMR spectrum of a 1 g/dL benzene or carbon tetrachloride solution of isomerized polymer is typically obtained on a 60- or 100-MHz spectrometer at one-half to one-third the normal scan rate. The cis-trans ratio is calculated from the relative intensities of the well-resolved signals of the cis- and trans-methyl
protons at 1.79 and 1.65δ, respectively, in benzene solution, and at 1.67 and 1.60δ, respectively, in carbon tetrachloride solution. The chemical shifts values (δ) are given relative to tetramethylsilane.

In the case of polybutadienes the determination of the cis-trans ratio has not been possible by ordinary (i.e., undecoupled) ¹H NMR spectroscopy at 60- or 100-MHz. However, suitable decoupling of the methylene proton signals for polybutadiene at 100 MHz permits not only a determination of cis-trans content but also the distribution of diads (cis-cis, cis-trans, trans-cis, trans-trans). Moreover, decoupling the olefinic proton signals at 300 MHz allows a determination of the cis-trans triad sequence distribution as well as the cis-trans ratio.

The advent of proton-decoupled ¹³C NMR spectroscopy has led to additional powerful methods for the analysis of both cis-trans content and sequence distributions in various polyisoprenes and polybutadienes. Indeed, recent microstructural studies with the aid of decoupled ¹H or ¹³C NMR spectroscopy have demonstrated that cis-trans isomerization of 1,4-polyisoprene or 1,4-polybutadiene results in random distributions of cis and trans units along the polymer chains.

D. Methods of Preparation

1. Methods of Isomerization

Polybutadienes can be isomerized in solution with ultraviolet light or γ-rays in the presence of suitable sensitizers including sulfides, disulfides, mercaptans, and organic bromine compounds such as allyl bromide. Unsensitized isomerization can occur on γ-irradiation of polybutadiene in solution or in the solid state, on ultraviolet irradiation of the polybutadiene film, or even thermally in the absence of a catalyst at temperatures below its decomposition temperature.

Cis-trans isomerization of polybutadiene also occurs in the course of vulcanization with sulfur at 140-160°, and under the influence of peroxides, nitrogen dioxide, sulfur dioxide, and selenium. The equilibrium cis-trans ratio in the photosensitized isomerization is about 25/75, and in the direct photoisomerization is about 30/70.

Natural rubber and gutta-percha can be isomerized by treatment with thiol acids, disulfides, butadiene sulfone, sulfur dioxide, and elemental selenium and photochemically with dibenzoyl disulfide, thiobenzoic acid, and diphenyl disulfide as sensitizers. The reactions can be carried in solution, in latex, or with thin sheets of either the raw or vulcanized polymers at 140° to yield equilibrium mixtures of similar isomeric composition, i.e., a cis-trans ratio of about 40/60. Polyisoprenes also undergo unsensitized photochemical and radiation-induced cis-trans isomerization.

With the organic sulfur compounds the isomerization probably occurs via a reversible step in a free-radical addition reaction. Isomerization is much more rapid with free thiol acid than with acyl or other disulfides.

It has been shown that cis-trans changes are the only structural alterations occurring during the reaction between natural rubber and sulfur dioxide at 140°, and a "clean" isomerized
polymer uncontaminated by adducts can be obtained only in this way. The isomerization presumably occurs via an "on-off" reaction at the double bond similar to that with the organic sulfur compounds, but free radicals are not involved because the rate of isomerization appears to be insensitive to free-radical catalysts and inhibitors.\textsuperscript{35}

A survey of photochemical, radiation chemical and assorted catalytic methods for cis-trans isomerization of polymers containing C=C bonds has been published.\textsuperscript{44}

References

1. Ames Research Center, Moffett Field, CA 94035.
2. Stanford Research Institute, Menlo Park, CA 94025.
4. The Natural Rubber Producers’ Research Association, Welwyn Garden City, Herts, England; current address - Universiti Sains Malaysia, Minden, Pulan Pinang, Malaysia.
22. Cunneen, J. I. The Natural Rubber Producers’ Research Association, Welwyn Garden City, Herts, England; current address - Universiti Sains Malaysia, Minden, Puluai Pinang, Malaysia.